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Effect of Intercalation in Graphite Epoxy Composites on the Shielding of High Energy Radiation

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ABSTRACT

The mass absorption coefficients of 13.0 keV x-rays, 46.5 keV γ-rays, and 1.16 MeV $\beta^{\ominus}$ particles have been measured for aluminum and for pristine and intercalated pitch-based graphite fiber composites. Intercalation was found to increase the mass absorption coefficient for ionizing radiation from 40 percent of the mass absorption of aluminum to 170 percent for bromine intercalation and 300 percent for iodine monobromide intercalation. The mass absorption coefficient for $\beta^{\ominus}$ particles of both the composites and aluminum was found to be 17.8 ± 0.9 cm^2/g. Inelastic scattering processes were significant in $\beta^{\ominus}$ particle shielding, and similar in all of the materials.

I. INTRODUCTION

Because of their low density and their exceptionally high strength and modulus, graphite fiber composites are increasingly being used for the fabrication of aircraft and spacecraft. They are replacing metals, such as aluminum (Al) alloys, which have poorer mechanical properties and higher densities. However, the replacement of metals in many electrical applications has proven to be difficult because the resistivity of graphite epoxy composites is typically three orders of magnitude higher than that of the metals they replace. Intercalation of graphite fibers, the insertion of guest atoms or molecules between the graphene planes, has been found to substantially lower the resistivity of the fibers, and hence the resistivity of fiber composites.[1]

One application for which these intercalated graphite composites have been proposed is electromagnetic interference (EMI) shielding covers. These covers comprise about 20 percent of the mass of the power system of a typical spacecraft. The projected mass savings from an exchange of intercalated graphite composite covers with the standard Al covers is in excess of 80 percent.[2] These calculations are based on mechanical properties being the limiting factor, which is the usual case. In certain environments, however, the limiting factor is the durability to high radiation environments. This radiation comes from cosmic rays, the solar wind (which is principally high energy protons and electrons), charged particles trapped within the radiation belts of earth or other planets, and other natural and man-made sources of high energy electromagnetic radiation.

High energy radiation is scattered principally by electrons, and so are best shielded by elements with high atomic number. Thus Al, with an atomic number of 13, is expected to shield better than graphite polymer composites, with an average atomic number near 6. Intercalation of graphite with high atomic number elements like bromine ($Z = 35$), and iodine ($Z = 53$) would be expected to increase the radiation shielding characteristics of graphite-polymer composites. Thus, the object of this work was to study the enhancement of the radiation shielding afforded to graphite fiber epoxy composites by the intercalation of graphite fibers with bromine (Br_2) or iodine monobromide (IBr).

II. METHODS AND MATERIALS

Thornel P-100 graphite fibers purchased from Amoco were selected for this study because of their availability and ease of intercalation. Br_2 intercalation was carried out in the vapor phase at room temperature. Epoxy composites were fabricated from these fabrics by Rohr Industries. Details of the intercalation, and composite fabrication and characterization are described elsewhere.[1]

Vapor phase intercalation of 2000 filament tows of P-100 by IBr was carried out at 60 °C for 48 hours. These fibers were then hand woven into 0° - 90° fabrics at a density of 10 tows per inch. Laminar composites were hand laid up using Master Mend Epoxy (Loctite Corp), which was chosen for its convenient setting time (90 min). Percent fiber volumes for these composites were appreciably lower than those of the Br_2 intercalated fiber composites because of the unavailability of a press. The composites were formed at room temperature between two glass plates on which weights were placed.

The thickness and density of each of the composite samples were determined using a micrometer and an analytical balance. Some of the properties of the composites are summarized in Table I. Note that the composite resistivity for the IBr intercalated fiber composite is very high compared to the Br_2 intercalated composite even though the fiber resistivity is lower. This is due to the low relative fiber volume of the IBr intercalated fiber composites, about 25 percent, as opposed to 48 percent for the Br_2 intercalated fiber composites. In well engineered composites it is expected that the resistivity would be similar to that of the Br_2 intercalated fiber composites.

A 40 μCi ^{210}Pb source was used to supply x-rays, γ-rays and high energy electrons. The decay scheme is shown below:

$$^{210}Pb \rightarrow {}^{210}Bi + 0.061\ MeV\ \beta^{\ominus} + 46.5\ keV\ \gamma\text{-ray}$$
$$^{210}Bi \rightarrow {}^{210}Po + 1.16\ MeV\ \beta^{\ominus}$$
$$^{210}Po \rightarrow {}^{206}Pb + 5.4\ MeV\ \alpha$$

Both ^{210}Bi ($t_{1/2}$ = 5 days) and ^{210}Po ($t_{1/2}$ = 138 days) were in secular equilibrium with ^{210}Pb ($t_{1/2}$ = 21 years). The α particle was not observed. The 0.061 MeV $\beta^{\ominus}$ was also not observed, but its interaction with the Pb 1s electron did give rise to a large flux of 13 keV x-rays.

Half thickness measurements for x-rays and γ-rays were made using a NaI(Tl) detector interfaced to a Nuclear Data ND2400 multi-channel analyzer (MCA). Both the 13.0 keV and the 46.5 keV γ-rays were monitored three times each over 10 sec intervals. This gave about 10^4 counts for the x-ray and about 10^5 counts for the γ-ray.

The source was placed about 8 cm from the detector, and stacks of one to nine ~1 mm thick composites were placed between them. The counts were corrected for background, but the correction for air displaced as each composite was added was found to be below the error of the measurement. The half-thickness was found by assuming exponential absorption and determining the least squares slope from semilog plots of the counts as a function of sample thickness. All of the plots were linear and predicted the data to within 1.0 percent (Figure 1). All of the count rates were well below detector saturation.

The absorption measurements for the 1.16 MeV electron were similar to those used for the x-rays and γ-rays except that they were measured *in vacuo* and the detector was an Ortec/EG&G Ultra detector with 6 keV resolution. The energy of the electrons is appreciably lowered even by a few inches of air, so the measurements

were done in a roughing vacuum (10^{-3} torr). Counts in the first 13 channels (energy below 100 keV) were dropped from the analysis because they contained a significant number of counts due to the 13 keV x-ray, and the 46.5 keV γ-ray peaks. The ^{210}Pb source saturated the detector when there were no absorbers present, so values of zero absorber thickness were extrapolated from the measurements of eight Al foils ranging in areal density from 48 to 175 mg/cm^2.

III. RESULTS AND DISCUSSION

X-Ray and γ-Ray Absorption

The half-thicknesses of Al, pristine fiber/epoxy composites, and composites made from Br_2 intercalated and IBr intercalated fibers for absorption of 46.5 keV γ-rays and for 13.0 keV x-rays are shown in Table II. The half thickness of pristine fiber composites was four times that of Al. That for Br_2 intercalated fiber composites was about 90 percent of Al. The half-thickness for IBr intercalated fiber composite was only 70 percent of that of Al despite the low fiber content. This table tells the shielding box thickness penalty or benefit which results from switching from Al if the application is ionizing radiation shielding limited. Typical shielding boxes are made from 2 mm (80 mil) Al. To have the same shielding from high energy electromagnetic waves, 8 mm thick pristine graphite epoxy boxes would be required, but only 1.8 mm Br_2 intercalated graphite epoxy boxes and less than 1.4 mm IBr intercalated graphite epoxy boxes would be required.

Usually, the savings of concern is not volume as much as it mass. Table III shows the mass absorption coefficient, the ratio of the linear absorption coefficient over the density (μ/ρ), for each of the materials. The (μ/ρ) is the mass of the material which is required to attenuate the intensity of the radiation by a factor of e (about 2.72).

The (μ/ρ) relative to Al illustrates the mass penalty or benefit that results if the spacecraft is to be operated in a high radiation environment. Thus, despite the higher strength, elastic modulus, and lower density of graphite epoxy composite, because it is so much less efficient at blocking high energy radiation, 2.4 times the mass of Al must be used to afford the same protection to a spacecraft operating in a high radiation environment. If Br_2 intercalated graphite fiber composites are used then only about 60 percent of the mass is required, and if IBr intercalated graphite composites are used then only about 34 percent of the mass is required to protect spacecraft in a high radiation environment. Clearly intercalation imparts major protection advantages for spacecraft exposed to high energy photons.

Intercalation with a high atomic mass number intercalate such as Br or I might be expected to improve the radiation shielding ability, that is, to shorten the half-thickness. Since the Br_2 intercalated fibers contain about 18 percent Br_2 by mass[3], that corresponds to about 3.3 percent by number. There is also a fiber volume expansion of about 10 percent[4]. This leads to an increase in the average atomic number of the composite to about 7.0, which leaves it well below the value of 13 for Al. Thus, it was somewhat surprising that the half-thickness of the Br_2 intercalated fibers composites were measured to be less than Al.

The density of the IBr intercalated fibers was measured to be 2.36 g/cm^3 using the density gradient method. This, along with the volume expansion, leads to a 24 percent intercalate by mass, also about 3.3 percent by number. The average atomic number for the IBr intercalated composites (neglecting hydrogens) is calculated to be 8.7, which is also less than the 13 of Al, yet the advantage is even greater than in the case of Br_2 intercalation. A few heavy atoms within a light matrix is a more efficient shield against high energy photons than a uniform, slightly more electron rich substance.

High Energy Electron Absorption

Analysis of the high energy electron data was complicated by the fact that a radioisotope was used for the electron source. Thus, unlike the photon experiment, the initial electrons were not monoenergetic. In addition, it was suspected that there would be a significant amount of inelastic scattering. Thus the total number of transmitted electrons over the energy region from 100 keV to 1.16 MeV was recorded.

It was found that the total number of electrons transmitted through the composite was a stronger function of areal density than of the particular shielding material. When the log of the rate electrons were transmitted through the various materials was plotted as a function of the areal density, (Figure 2) the data from all of the materials appear to fall along a single line. The slope of this line leads to a single mass absorption coefficient (μ/ρ) of 17.8±0.9 cm^2/g. It was noted that the two highest density points do not lie on the line because the count rates are comparable to background fluctuations.

A trace of intensity as a function of energy of electrons transmitted through one plate (118 mg/cm^2) and two plates (237 mg/cm^2) of pristine graphite epoxy composite from the multichannel analyzer is shown in Figure 3. Not only is there attenuation, but there is also a shift to lower electron energies due to inelastic scattering.

This shift in the distribution of electron energies was further quantified by breaking down the energy distribution into eight energy regions and sorting the transmitted electrons into them. The lowest energy region was then discarded because it contained the 13 keV x-ray and 46.5 keV γ-ray peaks which confused the analysis. A scale factor was calculated from the count rates between the electrons transmitted without absorbers, and those transmitted through one, two or three sheets. If the scattering was elastic, one would expect the modeled distribution to mirror the data. The result of these calculations for absorption by two absorbers is illustrated in Figure 4. Shown are the experimental count rates in each of the energy regions for two absorbers compared to the value predicted by calculating the scale factor times the unshielded energy distribution. The scale factor was flawed because it did not take into account those electrons whose energies would be shifted into region one, but the results are still instructive. The calculated value underestimated the number of low energy electron in regions 2-3, and overestimated the number of high energy electrons in regions 4-8. Thus it was clearly shown that inelastic scattering was significant in the propagation of high energy electrons through these materials.

The effect of intercalation on the inelastic scattering of electrons through graphite epoxy composites was difficult to determine because samples of pristine, Br_2 intercalated, and IBr intercalated composites of the same areal density were not available. Attempts were made to extrapolate the data to composites with a density of 0.300 g/cm^2. Br_2 intercalated composites were available with a density of .03056 g/cm^2; and IBr intercalated composites were available with a density of .2912 g/cm^2. Extrapolation to 0.300 g/cm^2 with these samples could be done with reasonable confidence, and they showed similar inelastic scattering. However, Pristine P-100 samples had to be interpolated between 0.2368 and 0.3526, and this could not be done with confidence. If a similar distribution of energies was assumed for the pristine fiber composites as for the intercalated, the results were reasonable. Thus no compelling evidence was found for intercalation affecting the inelastic scattering of the electrons.

In essence, intercalation enhances the shielding of high energy electrons solely by contributing to the density of the material. Of course, since the incident electrons are primarily scattered by electrons within the shield, the effect of intercalation is more precisely to add electrons to scatter the incoming particles. Not only do these materials lower the flux of high energy electrons, but those electrons which are transmitted are of lower energy, and thus, less likely to damage electrical components within the spacecraft.

From the perspective of spacecraft design, there appears to be no way to improve the specific shielding (shielding on a per mass basis) of electron shielding. The requisite areal density does not appear to be material dependent. That is, a greater thickness of a less dense material will be required to shield the same flux of high energy electrons. However, even a relatively poor shield is effective and will probably provide adequate protection in all but the most extreme environments.

IV. CONCLUSIONS

The half-thickness and mass absorption coefficient of 13.0 keV x-rays, 46.5 keV γ-rays, and 1 MeV electrons have been measured for pristine, Br_2 intercalated, and IBR intercalated pitch-based graphite fiber composites. For the x-rays and γ-rays, pristine graphite epoxy composites were found to have about 4.0 times the half-thickness, and 40 percent of the mass absorption for ionizing radiation than that of Al. Br_2 intercalation improved performance to 90 percent of the half-thickness, and 1.7 times the mass absorption coefficient of Al. IBr extended the performance to 70 percent of the half-thickness and 3.0 times the mass absorption of Al.

High energy electron absorption was found to be limited by the areal mass density of the shield, regardless of the material used for the shield. The mass absorption coefficient for all materials tested was $17.8 \pm 0.9\ cm^2/g$. Intercalation does increase the shielding of the composites, apparently by increasing their mass density. Inelastic scattering processes were found to be important but similar for all of the shielding materials.

Thus, intercalation not only makes up the deficiency conventional composites have in shielding components from ionizing radiation, but in the cases of Br_2 and IBr, actually confers an advantage over Al. Composites made from IBr intercalated graphite fibers can be made with one-third the mass of Al shields, or about 7 percent of the power system mass in those applications where shielding of ionizing radiation is the limiting factor. On the other hand, if shielding from high energy electrons is the limiting factor in a shield design, material choices cannot make an improvement.

V. ACKNOWLEDGMENTS

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VI. REFERENCES

1. J.R. Gaier, P.D. Hambourger, and M.E. Slabe, Carbon **29**, 313 (1991).
2. J.R. Gaier, IEEE Transactions on Electromagnetic Compatibility, 351 (1992).
3. C-C. Hung, Extended Abstracts: 17th Biennial Conference on Carbon, (American Carbon Society, St. Marys, PA, 1985) p. 82.
4. J.R. Gaier and D. Marino, Extended Abstracts: 17th Biennial Conference on Carbon, (American Carbon Society, St. Marys, PA, 1985) p. 8.

TABLE I -- Comparison of Properties of GIC-Epoxy Composites to Aluminum

	Fiber Resistivity μΩ-cm	Composite Resistivity μΩ-cm	Composite Thickness mm	Composite Density g/cm^3
Al	3	---	2.0	2.7
P-100	250	2010	0.75	1.61
Br_2	50	490	0.92	1.76
IBr	45	2460	1.90	1.35

TABLE II -- Half-Thickness of Shielding Materials

Material	46.5 keV γ-ray mm	13.0 keV x-ray mm	$\frac{T_{1/2}}{T_{1/2}\ Al}$
Al	7.5	4.2	1.0
P-100	30	17	4.0
P-100+Br_2	6.5	4.1	0.9
P-100+IBr	4.9	2.9	0.7

TABLE III -- Mass Absorption of EMI Materials

Material	46.5 keV γ-ray mm	13.0 keV x-ray mm	$\frac{(\mu/\rho)\ Al}{(\mu/\rho)}$
Al	.34	.61	1.0
P-100	.14	.25	2.4
P-100+Br_2	.61	.96	0.6
P-100+IBr	1.0	1.8	0.3

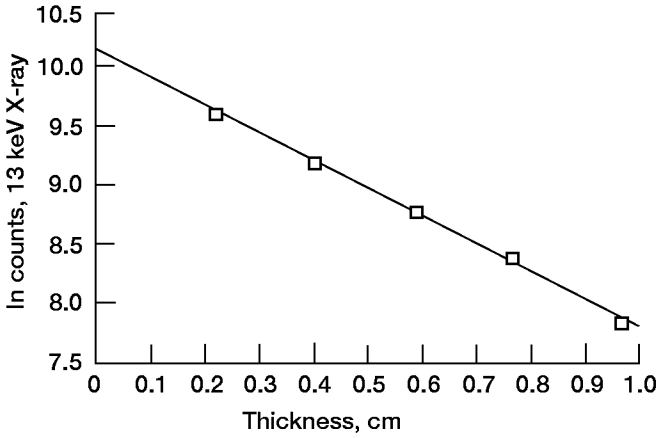

Figure 1.—Typical least squares plot used for the determination of half-thickness.

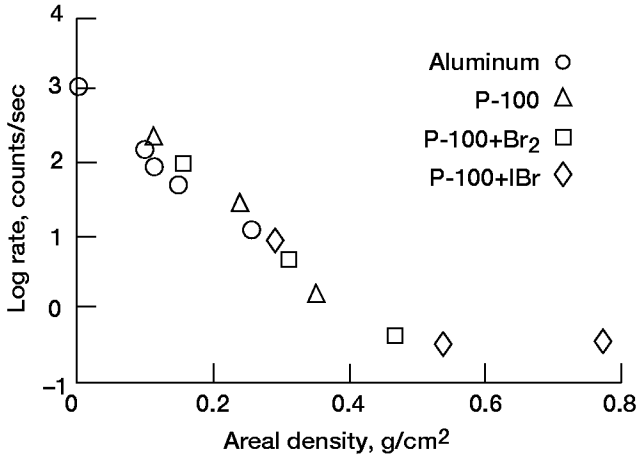

Figure 2.—The absorption of high energy electrons for several materials as a function of areal density falls along the same line, implying that electron absorption in this energy region is independent of Z.

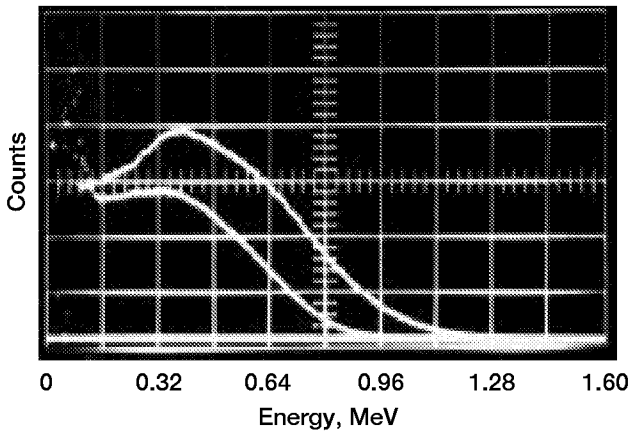

Figure 3.—Energy spectrum of β^- with 118 mg/cm^2 (upper line) and 237 mg/cm^2 (lower line) of graphite epoxy composite absorber.

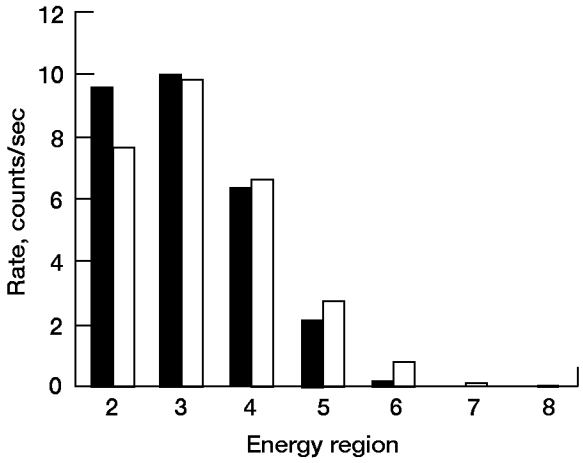

Figure 4.—Transmitted electron energy spectrum through a 0.236 g/cm^2 graphite epoxy composite (black) compared with that modeled by applying a scale factor to the unshielded energy distribution (white).

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13. ABSTRACT ***(Maximum 200 words)***

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